Recent Advances and Perspectives in Photodriven Charge Accumulation in Molecular Compounds: A Mini Review

Tobias H. Bürgin and Oliver S. Wenger*

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ABSTRACT: The formation of so-called solar fuels from abundant low-energetic compounds, such as carbon dioxide or water, relies on the chemical elementary steps of photoinduced electron transfer and accumulation of multiple redox equivalents. The majority of molecular systems explored to date require sacrificial electron donors to accumulate multiple electrons on a single acceptor unit, but the use of high-energetic sacrificial redox reagents is unsustainable. In recent years, an increasing number of molecular compounds for reversible light-driven accumulation of redox equivalents that do not need sacrificial electron donors has been reported. Those compounds are the focus of this mini review. Different concepts, such as redox potential compression (achieved by proton-coupled electron transfer, Lewis acid−base interactions, or structural rearrangements), hybrids with inorganic nanoparticles, and diffusion-controlled multi-component systems, will be discussed. Newly developed strategies to outcompete unproductive reaction pathways in favor of desired photoproduct formation will be compared, and the importance of identifying reaction intermediates in the course of multiphotonic excitation by different time-resolved spectroscopic techniques will be discussed. The mechanistic insights gained from molecular donor−photosensitizer− acceptor compounds inform the design of next-generation charge accumulation systems for solar energy conversion.
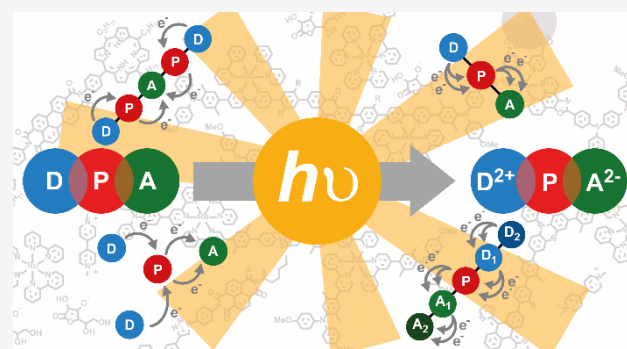
INTRODUCTION

The temporary accumulation of multiple redox equivalents is crucial for fuel-forming reactions from abundant low-energetic starting materials, such as water or carbon dioxide. Reduction of CO_2 by single-electron transfer is highly disfavored, whereas multi-electron redox processes can occur at moderate electrochemical potentials, particularly when coupled to proton transfer reactions.[1,2] Water splitting to hydrogen and oxygen requires the accumulation of two electrons on the reductive side and four electron holes on the oxidative side.[3] Natural photosynthesis can be seen as a blueprint for this overall process, and solar light as a very abundant energy source becomes very attractive for the formation of "solar fuels" with artificial systems.

Inorganic colloidal quantum dots (QDs) are suitable candidates for charge accumulation, and they combine several favorable properties, such as high molar extinction coefficients and greater photo-robustness than molecular systems.[4,5] On the other hand, there is usually a distribution of different QD sizes that can lead to a significant variation in the electronic properties of a QD ensemble, and there can be important surface and defect influences that complicate mechanistic insight into the photoinduced elementary processes occurring with QDs and nanocrystals.[6,7] Conversely, molecular systems with photosensitizer and electron donor and acceptor moieties

have very well-defined structures, making them well-suited for mechanistic studies, partly as a result of readily observable reaction intermediates using different (time-resolved) spectroscopic techniques. Until relatively recently, this approach has been mainly applied to investigate photoinduced single-electron transfer reactions, whereas photoinduced multi-electron transfer remained underexplored. In most cases of reporting the light-driven accumulation of multiple electrons on an acceptor moiety, sacrificial electron donors were used in large excess to ensure efficient photoreaction and to suppress undesired processes.[8−13] The decomposition of the radical intermediates of the sacrificial donors disfavors reverse electron transfer and, therefore, promotes the formation of the desired photoproducts. Such investigations with sacrificial reagents are important and useful for studying and optimizing catalytic reactions in an isolated way. Moreover, sacrificial reagents played a pivotal role in pioneering work on light-driven charge

accumulation in donor−acceptor compounds.[14,15] However, the use of sacrificial electron donors is incompatible with the goal of forming solar fuels in a sustainable manner, meaning that the development of systems that can reversibly accumulate multiple redox equivalents under light irradiation is necessary. The absence of sacrificial reagents makes the accumulation of redox equivalents much more difficult, yet the design of molecular systems can be varied across a broad range of combinations of different photosensitizers and electron donors and acceptors. Against this background, the focus of our mini review will be on molecular systems exploiting innovative strategies for the multi-photon-induced reversible charge accumulation in the absence of sacrificial electron donors.

■ COVALENT (D)PAP(D) MOLECULAR SYSTEMS

Initially aiming at molecular photoswitches, the groups of Wasielewski and Imahori independently synthesized and explored the porphyrin-based compounds in parts a and b of Figure 1.[16,17] These multi-component systems, reported in
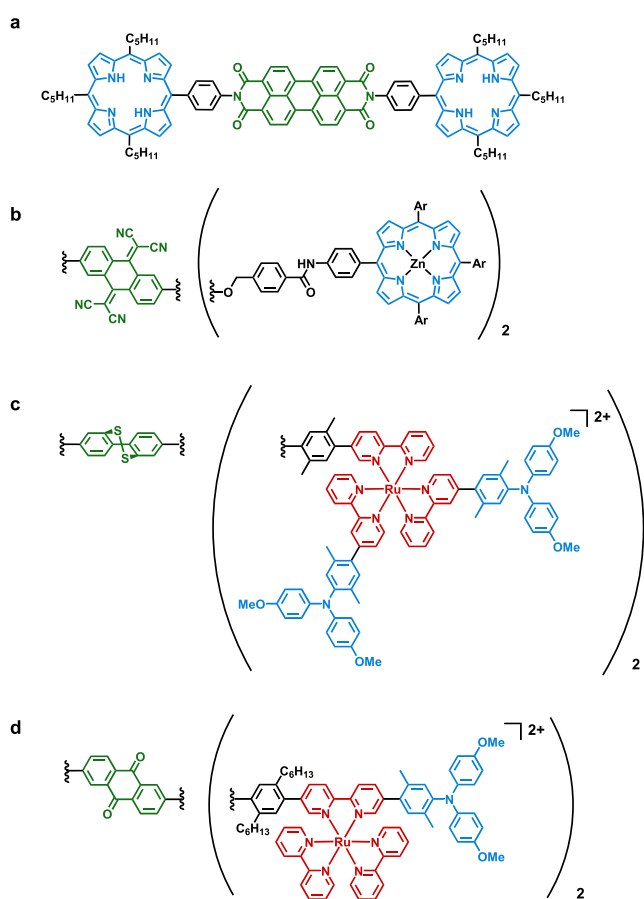

Figure 1. Molecular systems with central two-electron acceptors and multiple single-electron donors at the periphery.[16−19]

1992 and 1998, respectively, were among the very first examples of molecular compounds for photoinduced charge accumulation, which did not rely on sacrificial electron donors. Both compounds consist of a central two-electron acceptor (A) with two peripheral photosensitizers (P), each of which can act as a donor of a single electron upon photoexcitation. The compound in Figure 1a is comprised of a central perylene diimide (PDI) acceptor with two porphyrin (H_2P) sensitizers.

In pump−probe experiments with a picosecond laser, excitation of H_2P at 585 nm led to the formation of the $H_2P^{\bullet+}−PDI^{\bullet-}−H_2P$ photoproduct, which was observed under low-power excitation conditions. With the increase of the laser excitation density to the extent that up to 5 photons became available per molecule, the photoproduct $H_2P^{\bullet+}−PDI^{2-}−H_2P^{\bullet+}$ was identified by the characteristic absorption bands of PDI^{2-}, which strongly differ from the spectral features of $PDI^{\bullet-}$.

In the compound of Figure 1b, the central two-electron acceptor tetracyanoanthraquinonedimethane (TCAQ) is flanked by two zinc porphyrins (ZnP) photosensitizers.[17] After single-laser excitation at 532 nm, photoinduced electron transfer from one ZnP unit to TCAQ occurs, yielding $ZnP^{\bullet+}−TCAQ^{\bullet-}−ZnP$. A second laser pulse at 555 nm delayed by 233 ps excited the second (yet unreacted) ZnP unit, which further reduced $TCAQ^{\bullet-}$ to $TCAQ^{2-}$, yielding $ZnP^{\bullet+}−TCAQ^{2-}−ZnP^{\bullet+}$ as the final photoproduct. TCAQ undergoes strong geometric changes from a boat-like structure in its native (neutral) form to a planar aromatic system upon two-electron reduction, which causes potential inversion.[20] The authors tried to exploit this effect to obtain longer lifetimes for the $TCAQ^{2-}$ photoproduct compared to $TCAQ^{\bullet-}$, but the lifetime remained nearly unchanged with 1.5 ns for $ZnP^{\bullet+}−TCAQ^{2-}−ZnP^{\bullet+}$ compared to 1.2 ns for $ZnP^{\bullet+}−TCAQ^{\bullet-}−ZnP$. The authors furthermore noted that the spectral features of $TCAQ^{\bullet-}$ and $TCAQ^{2-}$ cannot be distinguished easily and that both reduction products have very similar ultraviolet−visible (UV−Vis) spectra with an absorption band maximum at 620 nm. According to other studies, the absorption maximum of $TCAQ^{2-}$ should be detectable at around 540 nm and, thus, should in principle be differentiable from the absorption spectrum of $TCAQ^{\bullet-}$.[21,22]

The concept of potential inversion on double-electron accumulation was also of central interest in a study performed by our group on a molecular heptad with dibenzo[1,2]dithiin (PhSSPh) as the central two-electron acceptor, flanked by two ruthenium(II)-based photosensitizers and four triarylamine (TAA) electron donors (Figure 1c).[18] Within the duration of one ~10 ns 532 nm laser pulse, both photosensitizers were excited into their emissive ^{3}MLCT state, which was reductively quenched by the covalently attached TAA electron donors. Both reduced photosensitizers subsequently donated their excess electron onward to the central PhSSPh acceptor (Figure 2). Single-electron reduction of PhSSPh is endergonic, and therefore, a stepwise pathway seemed rather unlikely, pointing toward a concerted two-electron reduction, although this mechanistic hypothesis could not be directly tested in the experiment. Be that as it may, the transient UV−Vis absorption spectroscopy clearly indicated the formation of PhS^-PhS^- and corroborated the formation of the desired two-electron photoproduct with an overall quantum yield of 0.5%.[18] In a structurally related triad in combination with triethylamine as the sacrificial electron donor, two-electron photocatalysis with an aliphatic disulfide substrate by disulfide−thiolate exchange under continuous illumination was accomplished.[23] The turnover number (TON) for the triad was 42, which is significantly higher than the TON of 4 for a comparable single-electron transfer catalyst explored under identical reaction conditions. Catalytically obtained thiolate can be regarded as the "solar fuel" model compound in this specific case. The use of a sacrificial electron donor was crucial in this case to demonstrate the potential of multi-electron catalysis, and the

Concerted Path   **Stepwise Path**
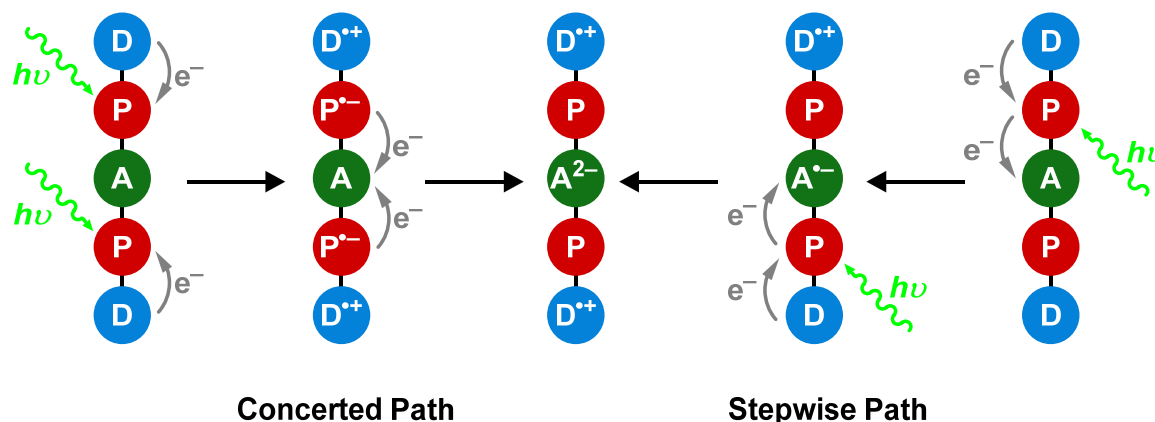
Figure 2. Schematic representation of a DPAPD system with possible reaction pathways for electron accumulation on the central acceptor unit (D = donor, P = photosensitizer, and A = acceptor).

concept of redox potential inversion was useful for that purpose.

When the structurally related pentad in Figure 1d is excited with an intense 532 nm laser pulse, doubly reduced anthraquinone (AQ) and two singly oxidized TAA units were observable by transient infrared (IR) spectroscopy.[19] Transient IR spectroscopy was much better suited to distinguish between $AQ^{\bullet-}$ and AQ^{2-} compared to transient UV−Vis spectroscopy. The $TAA^{\bullet+}−AQ^{2-}−TAA^{\bullet+}$ photoproduct had a lifetime of 870 ns in deaerated acetonitrile at room temperature, which is surprisingly long. It seems plausible that this is due to the inverted driving force effect, because the $TAA^{\bullet+}−AQ^{2-}−TAA^{\bullet+}$ photoproduct stores 3.56 eV of energy, while the overall reorganization energy for the thermal reaction back to the initial state is likely considerably lower. Stabilization of the final AQ^{2-} state by protonation led to an increase of the lifetime of the two-electron photoproduct to 4.7 μs but also to a decrease of the stored energy to 1.51 eV.[24] The stabilization of the intermediate state (in the form of $AQH^{\bullet}$) did lead to light-driven accumulation of redox equivalents in a stepwise consecutive process (Figure 2), but the reverse two-electron charge recombination seemed to occur in the form of a concerted two-electron–two-proton-coupled overall reaction.[24] The stepwise accumulation process is beneficial when using low-intensity excitation, for example, when considering sunlight as the excitation source. Without stabilization of the intermediate states by protonation, a second (subsequent) excitation is likely to induce energy-wasting reverse electron transfer.[25,26] Consequently, in the absence of protons that stabilize the intermediate, both photosensitizers need to be excited in parallel to accomplish two-electron reduction of the central acceptor, and this is only realistic under high-intensity (laser) irradiation. Even longer lifetimes, extending to the millisecond time scale, were achievable by stabilization of the AQ^{2-} photoproduct by Sc^{3+} and other Lewis acids by metal-ion-coupled electron transfer.[27,28] On this comparatively long time scale, bimolecular deactivation pathways interfered with unimolecular charge recombination even at micromolar concentrations of the molecular pentad, complicating mechanistic analysis.[28] Conceptually related two-electron transfer reactions were also reported for a structurally simpler compound with anthraquinone.[29]

COVALENT DPA MOLECULAR SYSTEMS

In the examples considered above, multiple photosensitizers and single-electron donors were attached to a central multi-electron acceptor to achieve reversible electron accumulation. For fuel-forming reactions, on the other hand, it would be highly desirable to accumulate electrons and holes on spatially separate units. The simplest fully integrated molecular structure for this task is a donor−photosensitizer−acceptor (DPA) triad, in which the donor and acceptor can both accumulate multiple charge equivalents. A schematic representation of such a structure is shown in Figure 3a. Absorption
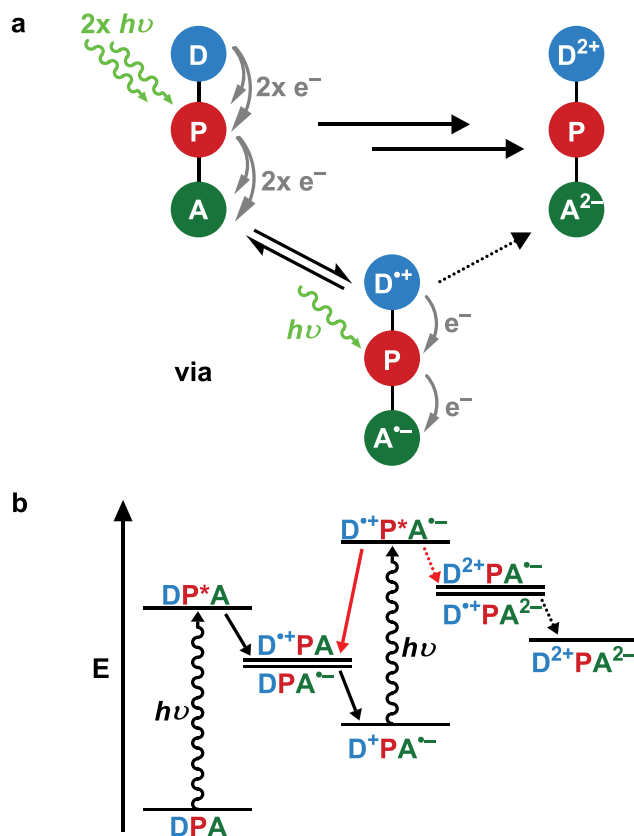
Figure 3. (a) Schematic representation of charge accumulation in a DPA system and (b) its respective simplified energy-level diagram.

of a photon by the central photosensitizer leads to the first charge-separated state $D^{\bullet+}PA^{\bullet-}$. If this first charge-separated state is sufficiently long-lived, a second photon can induce a secondary charge separation, leading to the formation of $D^{2+}PA^{2-}$. The overall process therefore resembles the natural photosynthesis Z-scheme, as illustrated in Figure 3b, although in the natural system, two different photosensitizers operate in series, while here only a single photosensitizer is present. In principle, the process in Figure 3b can be further repeated; however, all steps have to be thermodynamically favorable, and the photoredox properties of the photosensitizer dictate the choice of possible donors and acceptors (or vice versa). Typically, with increasing number of accumulated charges, the further reduction of acceptor units and the further oxidation of donor moieties become increasingly difficult. As seen above in the case of the compound in Figure 1d, stabilization effects, such as protonation of reduced species, metal-ion coupling, or structural rearrangements (leading to redox potential compression or inversion), can facilitate the accumulation of redox equivalents at the cost of a smaller amount of stored energy.

Ultimately, when aiming at the use of natural sunlight, the impact of photoexcitation over a broad wavelength range rather than monochromatic excitations will have to be considered. In the electronic ground state, typically only the photosensitizer absorbs in the visible range, whereas the electron donor and acceptor moieties often do not significantly absorb. This is usually not the case for the intermediate charge-separated states, such as, for example, $D^{\bullet+}PA^{\bullet-}$ in Figure 3b. Typically, $A^{\bullet-}$ and $D^{\bullet+}$ are open-shell radical species with strong absorptions over a significant portion of the visible spectrum. To some extent this is desirable, because it opens the possibility to detect these intermediates by transient UV–Vis absorption spectroscopy. On the other hand, direct excitation of these radicals can lead to fast unproductive charge recombination.[9,25,26,30] Therefore, absorption bands of intermediate species should ideally not overlap with the photosensitizer absorption in the targeted excitation region.

Undesirable charge recombination can furthermore take place after the selective excitation of the photosensitizer (*P) in a charge-separated state of the molecule. In DPA triads, *P is in close proximity to $A^{\bullet-}$ and $D^{\bullet+}$, which can lead to fast reverse photoinduced electron transfer from $A^{\bullet-}$ to *P or from *P to $D^{\bullet+}$. These undesirable events are represented by the solid red arrow in Figure 3b. This problem was directly addressed in the DPA compound shown in Figure 4.[31,32] The respective triad is not fully molecular but rather a hybrid system comprised of an oligotriarylamine (OTA) donor and a ruthenium(II) α-diimine photosensitizer attached to a TiO_2 acceptor. The very fast electron injection from the excited

Figure 4. DPA system for two-electron and two-hole accumulation, comprised of a molecular donor and a nanoparticle acceptor.[31,32]

photosensitizer to the TiO_2 acceptor was exploited to outcompete the above-mentioned unproductive reverse electron transfer processes. Thermal charge recombination occurred on the millisecond time scale after single-pulse 480 nm laser excitation of the overall triad. In a pump–pump–probe transient UV–Vis absorption experiment with a second 480 nm laser pulse delayed by 1 μs, the spectral features of OTA^{2+} were identified, representing unambiguous evidence for the desired photoproduct $OTA^{2+}-Ru(II)-TiO_2^{2-}$. After the first pump pulse, ~30% of all triads were excited and reacted onward to the $OTA^{\bullet+}-Ru(II)-TiO_2^{\bullet-}$ photoproduct. The yield of OTA^{2+} after the second pulse was ~10%, which corresponds to a nearly quantitative formation of the charge-accumulated state from the initially excited photosensitizer state.

A different concept to avoid undesirable reverse-electron transfer processes was explored in the purely molecular $D_2D_1PA_1A_2$ pentad of Figure 5a. After excitation of the central photosensitizer, reductive quenching of photoexcited P by D_1, or oxidative quenching by A_1, both of which are in close proximity to *P, can in principle occur. Subsequent electron or hole transfer from D_1 or A_1 regenerates P, and the first charge-separated state CSS1 ($D_2D_1^{\bullet+}PA_1^{\bullet-}A_2$) is reached after absorption of the first photon. Provided suitable molecular design and mutual adjustment of redox potentials, the hole on $D_1^{\bullet+}$ can now spontaneously transfer to D_2 and the electron on $A_1^{\bullet-}$ can transfer to A_2 to yield CSS2 without any further light absorption. For this to occur, D_2 has to be a stronger donor than D_1 and A_2 has to be a stronger acceptor than A_1. Following further excitation of P in the now formed $D_2^{\bullet+}D_1PA_1A_2^{\bullet-}$ intermediate, the hole and the electron are at this point at larger distance to *P, and therefore, undesirable reverse electron transfer (from $A_2^{\bullet-}$ to *P or from *P to $D_2^{\bullet+}$) should be less favored than the formation of CSS3. To reach the targeted CSS4, $D_2^{\bullet+}$ still has to be a stronger donor than D_1 and $A_2^{\bullet-}$ must be a stronger acceptor than A_1. This restriction strongly limits the possible donor, photosensitizer, and acceptor combinations and essentially requires D_2 and A_2 to be units with strongly compressed or even inverted redox potentials. D_1 and A_1 can be regarded as relays similar to the series of proton-coupled redox cofactors in photosystem II.[33,34] Because a complete molecular pentad system of this type can only be prepared with significant synthetic effort, to date only a simpler version in the form of a D_2D_1P triad system in combination with an external reversible electron acceptor was explored. Specifically, $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) as the photosensitizer was combined with phenothiazine (PTZ) as D_1, extended tetrathiafulvalene (ExTTF) as D_2, and methyl viologen (MV^{2+}) as the external electron acceptor (Figure 5b).[35] ExTTF was chosen because it fulfills all previously listed requirements, in particular because potential compression could be observed in cyclic voltammetry measurements. In pump–probe experiments with ~30 ps laser excitation at 532 nm of the triad in the absence of any external acceptor, fast laser-limited formation of $PTZ^{\bullet+}$ was detected, followed by slower (300 ps) formation of $ExTTF^{\bullet+}$ by electron transfer from D_2 to $D_1^{\bullet+}$. Evidently, ExTTF is oxidized by the initially formed $PTZ^{\bullet+}$, and the desired CSS2 photoproduct is indeed reached. To explore the possibility of light-driven charge accumulation on ExTTF, MV^{2+} was employed as an external reversible electron acceptor. In a pump–probe experiment, the formation of $ExTTF^{\bullet+}$ was indeed observed along with the formation of $MV^{\bullet+}$. However, neither excitation power-
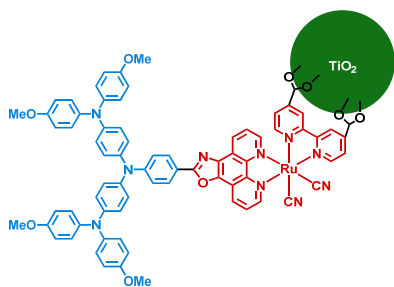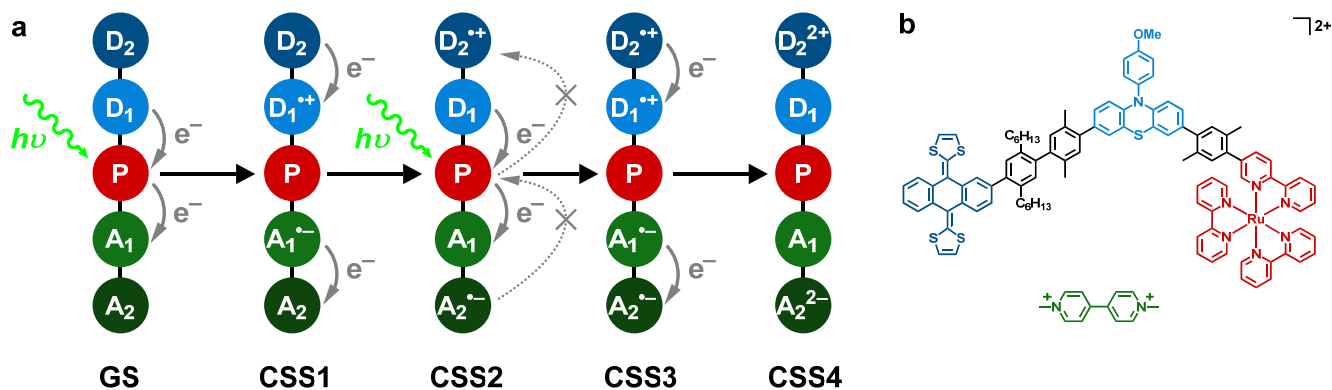
Figure 5. (a) Schematic representation of photoinduced charge accumulation in a $D_2D_1PA_1A_2$ system and (b) simplified realization in the form of a D_2D_1P triad with methyl viologen as the external electron acceptor.[35]

dependent studies nor two-pulse pump–pump–probe experiments provided any compelling evidence for the formation of ExTTF^{2+}. It seemed that the triad was not photostable enough for the formation of the desired photoproduct. A more chemically robust $D_2D_1PA_1A_2$ pentad system could therefore be a very interesting candidate for future investigations of the concept outlined by Figure 5a. Furthermore, PCET at the electron relays could potentially be exploited to stabilize intermediate states,[36] similar to the proton-coupled electron shuttle system present in natural photosynthesis.
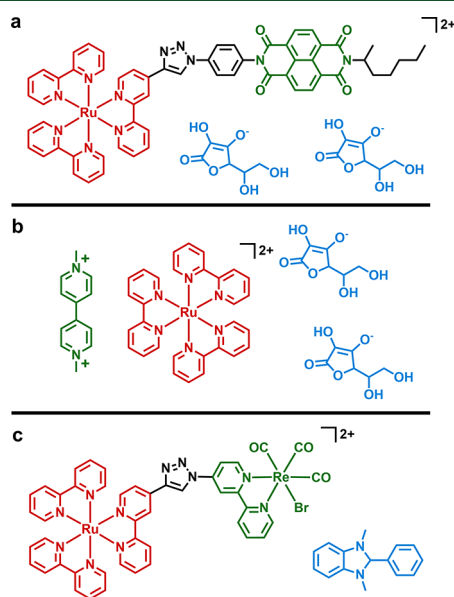
NON-COVALENT MULTI-COMPONENT SYSTEMS

Non-covalent multi-component systems have furthermore been successfully employed for electron accumulation, as exemplified by the compounds shown in Figure 6.[37−39] The

Figure 6. Multi-component systems for light-driven two-electron accumulation.[37−39]

system in Figure 6a is a dyad with a Ru(bpy)$_3^{2+}$ photosensitizer covalently linked to a naphthalene diimide (NDI) acceptor. Ascorbate was used as a reversible electron donor. In single 460 nm laser pulse transient absorption experiments, the characteristic UV–Vis absorption band of NDI$^{\bullet-}$ at 484 nm was observed, indicating the formation of the first charge-

separated state. Pump–pump–probe experiments with two consecutive 460 nm laser pulses delayed by 1 μs resulted in the formation of additional spectral features around 410 and 600 nm, which can be assigned to NDI^{2-}. After the first excitation pulse, ~33% of the triad molecules were promoted to the first charge-separated state containing NDI$^{\bullet-}$, and after the second laser pulse, 4% reacted onward to the second charge-separated state containing NDI^{2-}.[37] This overall quantum yield may seem low, but it should be kept in mind that biphotonic processes are inherently less efficient than monophotonic reactions.[40,41] In a structurally related system (not shown), in which a central NDI acceptor was covalently connected to two peripheral Ru(bpy)$_3^{2+}$ units with ascorbate as the electron donor, no charge accumulation product could be observed.[42] The same observation was made with covalently attached triarylamine electron donors, presumably because of rapid reverse electron transfer leading to efficient charge recombination. However, in combination with triethylamine as a sacrificial electron donor, charge accumulation on the NDI moiety was observed under continuous illumination.[42]

A completely non-covalent termolecular system for light-driven charge accumulation was comprised of a Ru(bpy)$_3^{2+}$ photosensitizer, MV^{2+} as an electron acceptor, and ascorbate as an electron donor (Figure 6b).[38] In the presence of an excess of ascorbate, which induced reductive excited-state quenching of Ru(bpy)$_3^{2+}$, the characteristic spectral features of MV$^{\bullet+}$ around 395 and 605 nm were observed after excitation with 460 nm laser pulses. Following a second 460 nm pulse delayed by 80 μs, a decrease of the MV$^{\bullet+}$ absorption at 605 nm was detected, indicating that some MV$^{\bullet+}$ disappeared. At the same time, there was increased absorbance around 395 nm, where both MV$^{\bullet+}$ and MV^0 are absorbing. After subtraction of the spectral contributions of MV$^{\bullet+}$, the remaining spectrum strongly resembled the absorption spectrum of MV^0, indicating that electron accumulation on methyl viologen has indeed occurred. This is a completely diffusion-controlled system, in which the lack of covalent connections between individual subcomponents disfavors undesired reverse electron transfer processes.[38] In early studies, MV^0 was postulated as the key intermediate in the photochemical debromination of vicinal dibromides, which is an overall two-electron process. In this case, MV^0 was formed as the disproportionation product of two photochemically generated MV$^{\bullet+}$ in a biphasic system.[43,44]

In the dyad shown in Figure 6c, Ru(bpy)$_3^{2+}$ is attached via a triazole linker to a Re(bpy)(CO)$_3$Br complex.[39] Rhenium(I) tricarbonyl diimines are known for their CO$_2$ reduction

capabilities.[45] Excitation of the $Ru(bpy)_3^{2+}$ photosensitizer of the dyad at 460 nm in the presence of excess ascorbate resulted in the formation of the one-electron reduced dyad and oxidized ascorbate. The authors noted that, instead of a narrow absorption band at 500 nm that would be attributable to the one-electron reduced Re complex, a broad absorption between 480 and 600 nm appeared. This was interpreted in terms of localization of the excess electron on the bridging ligand between the Ru and Re complexes. A pump–pump–probe experiment with two temporally delayed laser pulses at 460 nm did not result in any formation of the desired charge-accumulated state. This was explained by fast intramolecular reverse electron transfer that outcompetes the intermolecular reductive excited-state quenching of $Ru(bpy)_3^{2+}$ by ascorbate in the presence of the bridge ligand-localized excess electron. Nevertheless, in combination with sacrificial electron donors, the dyad was used successfully for photocatalytic CO_2 reduction under continuous illumination. The best results were obtained with 1,3-dimethyl-2-phenylbenzimidazoline (BIH) as the sacrificial electron donor. The radical intermediate formed after BIH oxidation can presumably drive a secondary electron without the need for additional light input.[39]

CHALLENGES AND PERSPECTIVES

In the majority of the recent studies on photoinduced charge accumulation, the focus remained on the observation of photoproducts and their decay pathways after excitation by short and comparatively intense laser pulses. In a typical pump–probe experiment, laser pulses of ~10 ns duration and an energy of ~10 mJ are used, which correspond to far higher excitation densities than in the solar photon flux. Sunlight-simulating excitation has only been sparsely addressed until now. One of the few pertinent examples was a hybrid system, similar to that in Figure 4, which consisted of TiO_2 nanoparticles with co-anchored multiple $Ru(dmb)_2(dcb)^{2+}$ photosensitizers (dmb = 4,4'-dimethyl-2,2'-bipyridine; dcb = 4,4'-dicarboxylic-2,2'-bipyridine) present with high surface coverage and bis(triarylamine) electron donor units adsorbed with low surface coverage.[46] Under sunlight-simulating low-intensity illumination, the formation of the doubly oxidized electron donor was observed. In fully molecular compounds, light-harvesting antenna systems could potentially compensate for low photon fluxes, similar to what has been accomplished, for example, with a dendrimer compound, in which an array of light-absorbing naphthalene units was attached to a central viologen core.[47] Excitation of the naphthalene units was followed by oxidative quenching by the viologen core to yield doubly reduced viologen. Another possibility was demonstrated in a multi-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) system, in which higher energy BODIPY A and lower energy BODIPY B subunits were linked via a carbohydrate platform in a 3:1 ratio.[48] Quantitative energy transfer from the BODIPY A subunits to the BODIPY B subunit was observed. Generally, in molecular compounds for photoinduced charge accumulation, an array of chromophores could harvest photons and transfer the absorbed energy to acceptors, which subsequently drive the redox chemistry. Biphotonic excitation is inherently less efficient that mono-photonic excitation as noted above, but recent studies of triplet–triplet annihilation upconversion are very encouraging, in that subsolar excitation densities sufficed for efficient upconversion.[49]

Figure 7 illustrates some of the design strategies that can be useful to accomplish light-driven charge accumulation followed
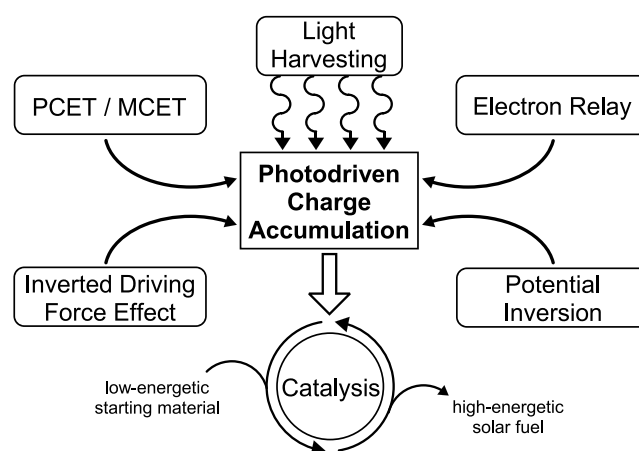
Figure 7. Design strategies to accomplish the production of solar fuels with molecular compounds.

by fuel-forming reactions. Direct exploitation of the accumulated charges in follow-up fuel-forming reactions remains a key challenge. The most sustainable source of electrons for such reactions would be water, which would necessitate that a catalytic system for water oxidation is coupled to the charge accumulation system, from where the reducing equivalents can subsequently be transferred onward to substrates, such as CO_2. In this ideal scenario, no sacrificial reductants would be necessary and the role of the charge-accumulating system would be essentially that of a relay between oxidation and reduction catalysts, which would likely operate at different rates. As long as this ideal case is not within reach, separate exploration and optimization of all three individual steps, namely, water oxidation, reversible charge accumulation, and CO_2 reduction, continue to be a meaningful research approach. In this context, recent studies of CO_2 reduction are very promising, for example, the use of Mn(I) complexes for the light-driven reduction of CO_2 to CO or HCOOH,[50] or the finding that an Fe(III) porphyrin-based system is able to catalyze the light-driven $8e^-$ reduction of CO_2 to methane.[51]

CONCLUSION

In recent years, different design strategies have been applied to accomplish photoinduced accumulation of multiple redox equivalents in molecular compounds without sacrificial electron donors. The majority of systems explored to date accumulate two negative charges on a two-electron acceptor, supplied by two independent single-electron donors. The only molecule-based system known thus far in which both multiple holes and multiple electrons have been simultaneously accumulated in a fully reversible manner (without sacrificial reagents) is a hybrid system comprised of molecular scaffolds attached to TiO_2 nanoparticles.[31,32,46] This illustrates the application potential of inorganic materials in the field of light-driven charge accumulation, although purely molecular systems remain very well-suited for mechanistic investigations. In particular, pump–pump–probe experiments have proven most valuable to understand productive and unproductive processes competing on the way to light-driven charge accumulation.[9,25,26,30] Such time-resolved experiments can provide essential insight into how sacrificial reagents can be made

unnecessary, to accumulate multiple redox equivalents in sustainable fashion. The concepts of redox potential compression or inversion seem particularly promising to facilitate the light-driven accumulation of redox equivalents based on the recent studies discussed herein.[18,52] Challenges that have only been sparsely addressed yet are light-harvesting for low-intensity light excitation and the use of the accumulated charges in multi-electron redox catalysis. These research fields have been successfully investigated in an isolated way, but the combination with a molecular compound for charge accumulation still requires major progress.

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Notes

The authors declare no competing financial interest.

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Oliver S. Wenger received his Ph.D. degree from the University of Berne (Switzerland) in 2002. Following postdoctoral stays at Caltech (2002−2004) and University of Strasbourg (2004−2006), he became an assistant professor at University of Geneva in 2006. In 2009, he moved to the University of Göttingen (Germany) as an associate professor. He returned to Switzerland in 2012 to the University of Basel, where he was promoted to full professor in 2018.

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■ NOMENCLATURE

A = electron acceptor
AQ = anthraquinone
BIH = 1,3-dimethyl-2-phenylbenzimidazoline
BODIPY = 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene
bpy = 2,2′-bipyridine
CSS = charge-separated state
D = electron donor
dmb = 4,4′-dimethyl-2,2′-bipyridine
dcb = 4,4′-dicarboxylic-2,2′-bipyridine
ExTTF = extended tetrathiafulvalene
H_2P = porphyrin
IR = infrared
MCET = metal-ion-coupled electron transfer
MV^{2+} = methyl viologen
NDI = naphthalene diimide
OTA = oligotriarylamine

P = photosensitizer
PCET = proton-coupled electron transfer
PDI = perylene diimide
PhSSPh = dibenzo[1,2]dithiin
PTZ = phenothiazine
QD = quantum dot
TAA = triarylamine
TCAQ = tetracyanoanthraquinonedimethane
TON = turnover number
ZnP = zinc porphyrin

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